Photoluminescence of nanosized Zn2SiO4:Mn depending upon preparation method

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Abstract. Nanosized Zn_2SiO_4:Mn powders were prepared by two different methods: a high-energy ball-milling of microcrystalline powder (so-called "top-down") and a sol-gel method ("bottom-up"). It was shown that it is possible to obtain particles of 30±10 nm by means of the ball-milling. A particle size of the Zn_2SiO_4:Mn synthesized by the sol-gel method ranged from 20 to 110 nm. It was found all samples exhibit photoluminescence (PL) in the green spectral region with a maximum emission wavelength from 515 to 520 nm. A nanopowder obtained by the ball-milling showed a significant decrease of the PL intensity comparing with bulk material. The PL intensity of the samples prepared by sol-gel method is much higher than that of ball-milled Zn_2SiO_4:Mn.

1. Introduction

Ability to manage the physical, mechanical, optical and other properties by changing the linear particle size causes a great interest in nanomaterials [1]. Manganese Mn^{2+} activated zinc orthosilicate, Zn_2SiO_4:Mn, is a well-known phosphor, which exhibits an intense green luminescence under UV light or electron beam. Decreasing of the particles to nanosize improves such important characteristics as the luminescence quantum efficiency, radiation resistance and adhesion to the substrate [2, 3]. Therefore, nanosized Zn_2SiO_4:Mn phosphor is perspective for a modern plasma and field emission panels, lights and other devices.

Currently, a lot of methods allowed to obtain nanomaterials on the "top-down" and "bottom-up" principles are described in literature. The first group includes methods wherein nanoparticles are obtained by milling of powder with an initial particle size of a few micrometers. The second group is nanoparticles formed from atoms and molecules during chemical reaction [4]. Each of the existing techniques has its own advantages and features. Thus, an important task is to identify the optimal method provided Zn_2SiO_4:Mn with the certain particle size and morphology and optical properties. In this work two methods of synthesis of nanosized Zn_2SiO_4:Mn were selected: high-energy ball-milling ("top-down") and sol-gel technology ("bottom-up").

The disintegration of the material by means of a high-energy ball-milling in mills of various designs is one of the simplest and most effective methods of the nanoscale achieving. This way allows obtaining the nanopowder with particles having a minimal size of about 20 nm from coarse-grained material [5, 6]. Since the process involves a high energy, it is important to study the influence of milling duration on the fluorescent properties of the material. In turn, the sol-gel technology makes

it possible to obtain multicomponent materials homogeneous on a molecular level and change the activator concentration in a wide range [7, 8].

Accordingly with the above, the aim of the present work was to reveal and study the PL features of the nanosized Zn_2SiO_4:Mn obtained by the two fundamentally different methods of nanotechnology.

2. Samples and experimental techniques

The Zn_2SiO_4:Mn microcrystalline powder with the activator concentration of 1.1 at. % and an average particle size of 3 μm was taken for disintegration. The ball-milling of the coarse-grained powder within 15, 30, 60, 120 and 240 min was carried out in a planetary ball mill *Retsch PM* 200. Isopropyl alcohol was used as a milling liquid. At the end of the process it was removed by drying. In addition, the nanopowders obtained by milling longer than 60 min were annealed in air at 300 ºC for two hours to relax the residual stresses and partially remove the adsorbents. Other ball-milling parameters were described in details in [9].

Zinc and manganese chlorides and tetraethoxysilane were used as precursors for preparation of Zn_2SiO_4:Mn sol. The activator Mn^{2+} concentration was 1.0 at. %. Gelation occurred at room temperature, after that the gel was dried to remove the liquid phase. Since the resulting material does not possess an ordered crystalline structure, powder subjected to annealing to obtain a crystalline modification of α-Zn_2SiO_4. Annealing was occurred in air at temperature range from 500 to 1200 °C in steps of 100 °C and hold for two hours at each temperature.

The Zn_2SiO_4:Mn nanopowders obtained by methods described above have been characterized by the crystal structure, phase composition and particle size. X-ray diffraction studies of coarse-grained and disintegrated Zn_2SiO_4:Mn revealed that the process duration does not affect the crystal structure of the samples. Significant broadening of the diffraction peaks, indicating a particle size decrease, is observed after 15 min of milling. It should be noted that impurity phases have not been detected in the samples. Crystallinity and phase composition of the Zn_2SiO_4:Mn obtained by sol-gel method, on the contrary, essentially depend on the annealing temperature. As expected an increasing of the crystallinity degree of the material, gradually decreasing of the amorphous phase amount, and increasing of α-Zn_2SiO_4 content were observed with increasing of annealing temperature. The impurity phases of ZnO and SiO_2 were detected in the samples (Table 1). The average particle size of the material was determined by the broadening of the diffraction peaks by Williamson-Hall method. As seen from table 1, the amount of nanoparticles in the disintegrated powder increased significantly with increasing of the process duration. The minimal particle size was 30 ± 10 nm. In Zn_2SiO_4:Mn obtained by sol-gel method a gradual coarsening of the particles occurs with increasing of annealing temperature.

Table 1. Particle size and crystallinity of Zn_2SiO_4:Mn produced by ball-milling and sol-gel methods

Ball-milling		
Milling time, t (min)	Particle size, D (nm)	Relative volume fraction of nanoparticles, V_{nano} %
15	70 ± 20	40
60	50 ± 10	80
120	30 ± 10	100
240	30 ± 10	100
Sol-gel		
Annealing temperature, T (ºC)	Particle size, D (nm)	Relative volume fraction of crystalline phases, V_{cryst} %
As dried at 220	20 ± 10	Amorphous
600	70 ± 15	Zn_2SiO_4 – 94, ZnO – 6

800	85 ± 15	Zn_2SiO_4 – 95, ZnO – 5
1000	90 ± 10	Zn_2SiO_4 – 97, ZnO – 3
1200	110 ± 10	Zn_2SiO_4 – 82.5, SiO_2 – 14.7, ZnO – 2.8

PL of obtained samples was studied using the *Perkin Elmer LS*55 spectrometer. The spectra registration was carried out in the mode of phosphorescence, the delay time was 1 ms, the wavelength of the exciting radiation λ_{ex} = 250 nm. Monochromator slit width was chosen depending on the luminescence intensity of the samples.

3. Results and discussion

Optical properties of an ion-activator are mainly determined by the crystal structure of the host matrix. *α*-Zinc orthosilicate crystallizes in the trigonal system (space group *R*-3*m*) and its structure is formed by $[SiO_4]^{4-}$ and $[ZnO_4]^{6-}$tetrahedra. When Mn^{2+} ions (electronic configuration $3d^5$) are injected into the matrix, they occupy positions of zinc Zn^{2+} in the lattice. The splitting of 3*d*-energy sublevels of ion activator occurs under the influence of a weak crystal field. Excitation by UV light leads to the transfer of charge carriers from the ground state of Mn^{2+} ($^6A_1$) to the conduction band (CB) of Zn_2SiO_4:Mn. From this, the electrons move to an excited state of the Mn^{2+} ion ($^4T_1$) by nonradiative transition. Relaxation of electrons to the ground state ($^4T_1 \rightarrow {}^6A_1$) causes intense luminescence with emission maximum in the range from 510 to 520 nm.

Figure 1 shows the excitation PLE (*a*) and emission PL (*b*) spectra of microcrystalline and disintegrated Zn_2SiO_4:Mn powders. The excitation spectrum of a microcrystalline powder has a broad band in the range from 220 to 360 nm with several maxima near 245, 260, 280 and 340 nm. According to [10], the first three bands belong to the electronic transition from the ground state ($^6A_1$) of Mn^{2+} to the CB of the host. An intense band with a maximum at 340 nm corresponds to the *d*-*d* transition of the activator ion. As seen in figure 1, *a*, after milling the shape of the spectrum does not change, but the intensity decreases significantly.

The emission spectrum of Zn_2SiO_4:Mn shows that the microcrystalline material has the highest intensity of luminescence (figure 1, *b*). As mentioned above, the intensity and position of the PL bands greatly influenced by the crystalline environment of the activator ion. Since the disintegration of microcrystalline Zn_2SiO_4:Mn does not affect the crystal structure, the main reason of PL quenching can be considered the presence of strong deformation destruction of particles that leads to the appearing of the dislocation network. Residual strain may change the crystalline field near Mn^{2+} ions, leading to decomposition of the matrix-activator solid solution. The PL quenching may occur due to diffuse redistribution of activator ions to dislocations arising during milling process. [11].

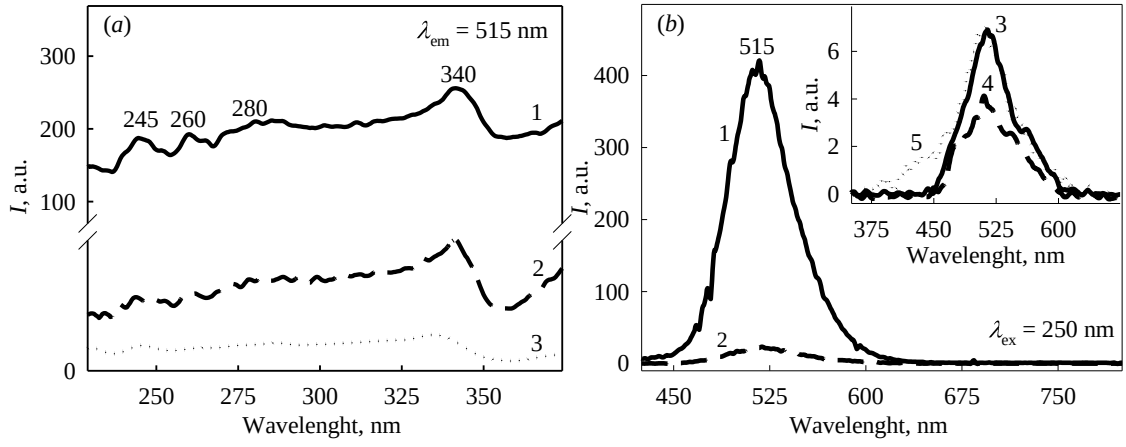

Figure 1. PLE (*a*) and PL (*b*) spectra of coarse-grained Zn_2SiO_4:Mn powder (1) and nanopowder

after ball-milling within 15 min (2); 120 min (3); 240 min (4); sample (4) annealed at 1100 ºC – (5).

Since annealing of disintegrated Zn_2SiO_4:Mn at 300 ºC does not influence the PL spectral characteristics, samples were further annealed at 1100 ºC. The inset in figure 1, *b* shows that high-temperature annealing promotes partial recovery of the PL (curves (4) and (5)), but the intensity of the emission is still much lower than that of the bulk powder. Maximum of the emission wavelength of the samples is at 517 ± 3 nm, that corresponds to an electronic transition $^4T_1 \rightarrow {}^6A_1$.

In turn, Zn_2SiO_4:Mn obtained by sol-gel method also shows the dependence of the PL properties upon the preparation conditions. The emission of the material is not observed up to the annealing at 600 ºC. Figure 2 shows that the intensity of the bands in the excitation and emission spectrum increases significantly with increasing of annealing temperature. The change is associated with crystallinity improving of the material and the gradual increase of the Zn_2SiO_4:Mn phase content. In this case, one can say of a homogeneous distribution of the activator ions in the host and the formation of a solid solution of Mn^{2+}-Zn_2SiO_4. The excitation spectra of the samples are presented by a broad band in the range from 220 to 300 nm with three maxima at 230, 250 and 260 nm (figure 2, *a*). The last two peaks indicate the transfer of energy from the ground level of Mn^{2+} ion to the CB of the host. It can be assumed that the presence of the band with maximum at 230 nm and a further sharp intensity increase toward short wavelengths indicate the absorbance of the Zn_2SiO_4 matrix itself [12, 13].

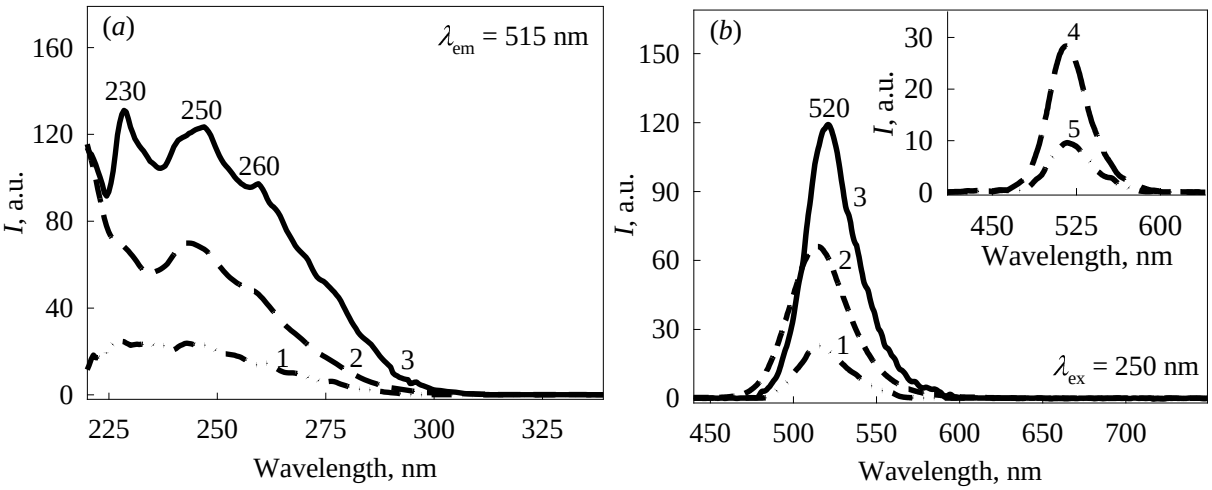

Figure 2. PLE (*a*) and PL (*b*) spectra of Zn_2SiO_4:Mn synthesized by sol-gel method and annealed at 600 ºC (1), 700 ºC (2); 900 ºC (3); 1100 ºC (4); 1200 ºC (5).

Samples prepared by the sol-gel technology, exhibit only a narrower band emission with a maximum at 518 ± 2 nm (figure 2, *b*). It is important to note that after annealing at temperatures above 1000 ºC there is a significant decrease in the intensity of luminescence. Explanation for this would be the changing of the coordination of the activator ions. In Zn_2SiO_4:Mn annealed at temperatures up to 1000 ºC a gradual increase in the symmetry of the crystal field around Mn^{2+} ions occurred, that led to an increase in the PL intensity. On the other hand, the absence of SiO_2 impurity phase is observed at higher temperatures (table 1). Due to that the tetrahedral coordination of the activator ions can be significantly distorted, resulting to the appearance of nonradiative recombination centers. Similar phenomenon was reported in [14].

4. Conclusion

In this work Zn_2SiO_4:Mn nanopowders were prepared by means of "top-down" and "bottom-up" methods. The samples were characterized by the particle size and crystal structure. PL properties of the Zn_2SiO_4:Mn were studied depending on the preparation conditions: milling duration and annealing temperature. Despite the fact that the disintegrated material is characterized by small particle size, high energy process causes significant deformation of the crystal lattice and degradation of the PL. The additional high-temperature annealing does not ensure recovery of the emission intensity. Thus, while using high-energy milling it is possible to achieve a narrow size dispersion of nanoparticles, this method is not effective enough for production of studying phosphor.

The PL of Zn_2SiO_4:Mn obtained by the sol-gel process has an intense band in the green region of the visible spectrum. Dependence of the luminescence intensity on the annealing temperature is observed. In addition, one of the features is a coarsening of nanoparticles during annealing. The sol-gel method can be considered more promising to obtain the luminescent nanomaterials than ball-milling. It is needed further improvement of the sol-gel method for the synthesis of nanosized phosphors with narrow particle size dispersion, good crystallinity and high luminescence intensity.

Acknowledgments

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